Relevance of electron transfer mechanism in electrocatalysis: the reduction of organic halides at silver electrodes

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The mechanism of dissociative electron transfer (ET) to a series of organic chlorides has been investigated both at an inert electrode and at a catalytic surface such as Ag; electrocatalysis is important only when breaking of the carbon–halogen bond is concerted with the ET.

Heterogeneous electrocatalysis, which is an important field of electrochemical science in continuous growth, covers a very wide range of topics such as, for instance, fuel cell technology, water electrolysis, Cl_2 production, organic electrosynthesis and pollution abatement.[1] Electrocatalytic reduction of organic halides (RX) has been a central topic in organic electrochemistry for the last few decades.[2] The process has received much attention both from mechanistic and synthetic view points. Among various examined electrode materials, silver has been found to possess extraordinary electrocatalytic properties.[3] Such electrocatalytic properties have been exploited in a few cases for synthetic[4] and environmental[5] applications, especially the abatement of organic pollutants such as greenhouse gases and bromophenols.

The mechanism of the electrocatalytic reduction of RX at Ag is still a subject of investigation. As reported so far, the most important factors affecting the catalytic properties of the metal are the type of the halogen atom,[3a,b] the molecular structure of RX,[3a,c] the surface morphology of the electrode[6] and adsorption/desorption behaviour of the halide ions X^-.[6b] A very important issue that has not been hitherto addressed is the relation between catalysis and the mechanism of electron transfer (ET) to RX. There are two possible mechanisms for the reductive cleavage of the C–X bond. ET and bond breaking can occur either in a stepwise manner with the intermediate formation of a radical anion (eqn (1) and (2)) or in a concerted way yielding directly a radical and an anion (eqn (3)).

$$RX + e^- \rightleftarrows RX^{\cdot -} \tag{1}$$
$$RX^{\cdot -} \rightarrow R^{\cdot} + X^- \tag{2}$$
$$RX + e^- \rightarrow R^{\cdot} + X^- \tag{3}$$

Since the dynamics of the dissociative ET to RX will be affected by electrocatalysis, careful investigation of the mechanism of ET at Ag may shed light on the origin of the catalysis at such a metal surface. In this communication we wish to report on the existence of a strong linkage between electrocatalysis and the mechanism of

dissociative ET. We investigated the reduction mechanism of a series of organic chlorides (Scheme 1) at silver and glassy carbon (GC) electrodes. The latter, which is considered to be the best approximation of an outer-sphere electron donor, was used to obtain reference data pertaining to a non-catalytic system.

All compounds exhibit similar voltammetric features at the two electrode materials.† Compounds **1**, **2**, **3**, **4** and **5c** exhibit a series of peaks (at least two), the first of which is always irreversible while the second is reversible. In contrast, compounds **5a**, **5b**, **6** and **7** show only one irreversible reduction peak up to the cathodic background limit. Fig. 1 shows examples of cyclic voltammograms
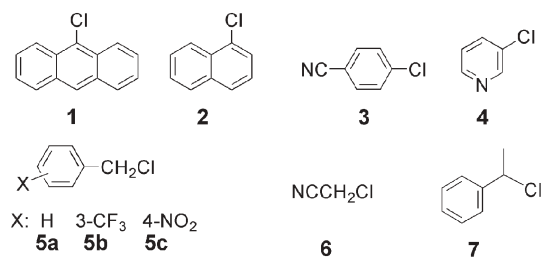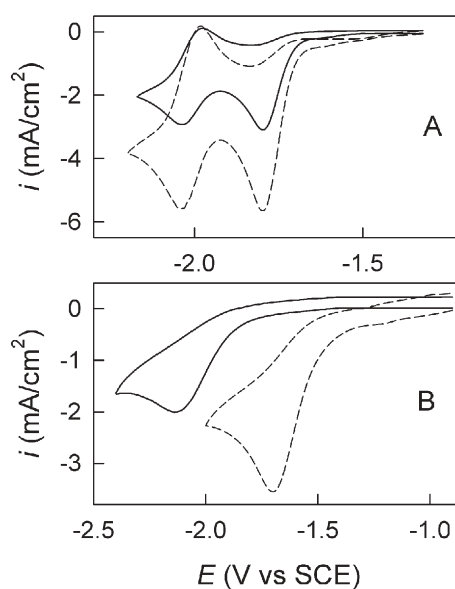

Scheme 1

Fig. 1 CVs of **1** (A) and **5a** (B) (0.002 M) recorded at 0.2 V s⁻¹ in CH_3CN + 0.1 M $(C_2H_5)_4NBF_4$ at GC (full lines) and Ag (dashed lines) electrodes.

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obtained for the two classes of compounds at GC and Ag electrodes. The electrochemistry of the organic halides **1–7** at inert electrodes is well documented in the literature.[7–9] The first peak involves reductive cleavage of the carbon–chlorine bond, whereas other successive peaks, when they are present, are due to the reduction of the product of the first reduction process, for example, anthracene[8c] in the case of **1** or 4,4′-dinitrobiphenyl[8a,9a] in the case of **5c**. These processes are not sensitive to the nature of the electrode material (Fig. 1A) and hence are of little interest to our investigation. We will therefore only focus our attention on the first irreversible reduction peak of each compound. It is worth noting, however, that non-halogenated compounds are not catalytically reduced at the Ag surface.

The voltammetric data, which were obtained at both electrodes with the appropriate correction of the solution resistance, are summarised in Table 1. Comparison of the peak potentials recorded at Ag and GC shows that reduction of compounds **1**, **2**, **3**, **4** and **5c** is insensitive to the type of electrode; practically identical E_p values are obtained at the two electrodes for these halides. Conversely, significantly more positive E_p values were obtained for **5a**, **5b**, **6** and **7** at Ag than at GC. Since GC can be considered to be an inert electrode material for the reduction of organic halides, the positive shifts observed at Ag are to be attributed to the electrocatalytic properties of such a cathode. At both electrodes, the peak potential and the peak current vary linearly with log v and $v^{1/2}$, respectively. The shape of the voltammetric peaks and the linear dependence of their peak currents upon $v^{1/2}$ indicate that at both electrodes the compounds undergo an overall reduction process under mass-transfer control.[10]

A simple approach in the investigation of the reductive cleavage mechanism (concerted *versus* stepwise) consists in the observation of the dependence of E_p on v and of the values of the half peak width, $E_{p/2} - E_p$. In the case of a concerted mechanism E_p varies linearly with log v with a slope $\partial E_p/\partial \log v = -29.6/\alpha$ mV at 25 °C, whereas $E_{p/2} - E_p = 47.7/\alpha$ at the same temperature.[11] In the stepwise mechanism, the values of $\partial E_p/\partial \log v$ and $E_{p/2} - E_p$ depend on the rate-determining step. At 25 °C the values of the slope and half peak width are −29.6 mV and 47.7 mV, respectively, if the cleavage reaction (eqn (2)) is the rate determining step.[11] If, instead, the ET (eqn (1)) is rate determining, $\partial E_p/\partial \log v = -29.6/\alpha$ mV and $E_{p/2} - E_p = 47.7/\alpha$ as in the case of the concerted mechanism.

Analysis of the voltammetric data recorded in a wide range of scan rates (0.05–10 V s^{-1}) yields the slopes and $E_{p/2} - E_p$ values reported in Table 1. It is worth noting that the reported data have not been corrected for the effect of the potential drop through the diffuse layer, *i.e.*, the Frumkin effect. However, whereas the Frumkin correction affects remarkably k^o of the ET,[10] it has a very modest influence on the value of α.[12] Therefore, for our purpose of mechanistic analysis the apparent values can be fairly used.

The values of the parameters calculated for compounds **1–3** are comparable with the theoretical values for a stepwise mechanism under kinetic control of the cleavage reaction. Undoubtedly reduction of such compounds occurs according to a stepwise mechanism. The assignment of the mechanism for the remaining compounds of the series is less straightforward. A helpful parameter in such a case is the transfer coefficient α. In fact, it is well known that the concerted ET mechanism is characterised by very small values of α (typically around 0.3), which indicates that the reduction potential is much more negative than the standard potential. This is predicted by the dissociative ET theory and is supported by a large number of experimental examples.[7,9,12] On the other hand, in the stepwise ET the process often occurs around its E^o and may be even positively shifted with respect to E^o because of the bond fragmentation reaction following the ET.[8]

The values of α calculated from $\partial E_p/\partial \log v$ and $E_{p/2} - E_p$ are included in Table 1. The values for compounds **1–3** are missing because, since reduction of such compounds follows a stepwise mechanism under kinetic control of the cleavage reaction, neither $\partial E_p/\partial \log v$ nor $E_{p/2} - E_p$ can be used to determine α. A survey of the data reported in Table 1 shows that the α values calculated for compounds **4** and **5c** are significantly greater than 0.5. The dissociative ET to these chlorides follows a stepwise mechanism. For all other compounds very small values of α are obtained indicating that ET and bond breaking are concerted.

The results of the mechanistic analysis reported here are in good agreement with literature data.[7–9,12] It is well established that ET to aliphatic halides follows a concerted mechanism; σ* radical anions are not formed because the concerted pathway is energetically more favourable. On the other hand, aromatic halides have low lying π* orbitals. Thus, transient radical anions are formed upon 1e$^-$ injection and the cleavage step may be viewed as an intramolecular dissociative ET. In the case of **5c**, the electron can be initially accommodated on the nitro group followed by

Table 1 Data for the electrochemical reduction of RCl in CH$_3$CN + 0.1 M (C$_2$H$_5$)$_4$NBF$_4$ at GC and Ag electrodes

RCl	GC					Ag					mechanism[e]	$E_p^{Ag} - E_p^{GC}$/V
	E_p^a /V	$E_{p/2} - E_p^b$ /mV	α^c	$\partial E_p/\partial \log v$/mV	α^d	E_p^a /V	$E_{p/2} - E_p^b$ /mV	α^c	$\partial E_p/\partial \log v$ /mV	α^d		
1	−1.79	53		−34		−1.79	51		−32		sw	0
2	−2.16	55		−33		−2.19	56		−34		sw	−0.03
3	−1.97	60		−34		−1.95	60		−32		sw	0.02
4	−2.25	62	0.77	−39	0.76	−2.28	67	0.71	−44	0.67	sw	−0.03
5a	−2.13	144	0.33	−92	0.32	−1.70	121	0.39	−84	0.35	c	0.43
5b	−2.04	118	0.40	−139	0.21	−1.66	134	0.36	−117	0.25	c	0.38
5c	−0.91	63	0.76	−42	0.70	−0.92	67	0.71	−44	0.67	sw	−0.01
6	−1.98	137	0.34	−113	0.26	−1.39	182	0.26	−112	0.26	c	0.59
7	−2.22	170	0.28	−134	0.22	−1.87	180	0.26	−124	0.24	c	0.35

[a] Peak potentials were measured at 0.2 Vs^{-1} and are reported *versus* the saturated-calomel electrode. [b] Average of the values obtained at different scan rates in the 0.05–10 V s^{-1} range. [c] Calculated from $E_{p/2} - E_p = 1.857 \, RT/F\alpha$. [d] Calculated from $\partial E_p/\partial \log v = -1.15 \, RT/F\alpha$. [e] Dissociative ET mechanism: stepwise (sw) or concerted (c).

intramolecular ET to the σ* orbital, thus giving a stepwise mechanism.

Examining now the electrocatalytic effect of Ag in relation to the mechanism of the reductive cleavage of the carbon–halogen bond, it becomes clear that catalysis occurs only when the concerted mechanism prevails. When the reductive cleavage of RCl passes through the intermediate formation of RCl·⁻, as well as when non-halogenated compounds are considered, the reduction process is insensitive to the nature of the electrode material. The process occurs by an outer-sphere ET mechanism without significant interaction of RCl and RCl·⁻ with the electrode surface.

The extraordinary electrocatalytic effect of Ag towards reduction of organic halides is probably related to the high affinity of the metal for the halide ions, which is well documented in literature.[13] Such an affinity, however, appears to produce no effect unless ET to RX involves concerted rupture of the C–X bond. It appears therefore that catalysis is driven by kinetics rather than by thermodynamics. The dissociative ET at Ag may be viewed as depicted in Fig. 2. It involves a transition state where an activated complex interacting with the electrode surface is formed. In the activated complex, the C–Cl bond has been considerably weakened because of the Cl···Ag and R···Ag interactions. The starting molecule and the ET fragments may or may not be involved in interactions with the electrode surface. The fact that identical reduction potentials are obtained for some RCl molecules at Ag and GC together with the linear variation of the peak current with $v^{1/2}$, observed for all compounds, suggest that RCl does not give significant interactions with the electrode. As to the ET products, presumably adsorbed Cl⁻ ions are formed, although they may be immediately expelled from the negatively charged electrode surface because of electrostatic repulsion.

Fig. 2 also shows a free energy diagram of the dissociative ET. We assume a very weak interaction of the reagents and products with the Ag surface. Because of the strong interaction of RCl with Ag at the transition state, the free energy of the activated complex is signi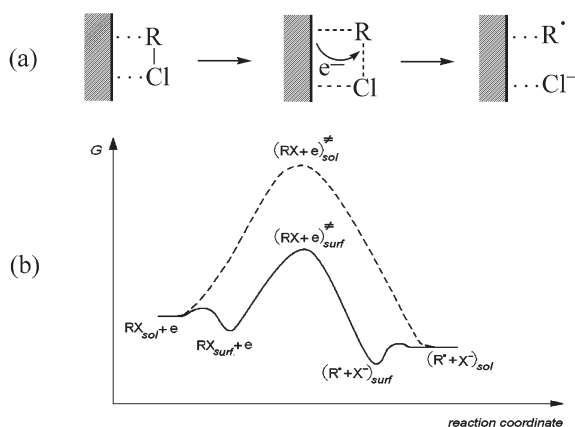ficantly lowered with respect to the outer-sphere ET path (dashed curve). This results in a remarkable decrease of the activation free energy of the catalysed pathway.

In conclusion we have shown that the reductive cleavage of C–Cl in a series of organic chlorides at Ag is strongly influenced by the mechanism of the dissociative ET. Although the catalytic properties of Ag originate from its affinity for the halide ions, the possibility of catalysis is linked to the concerted nature of the ET. It would be of interest to extend this type of investigation to bromides and iodides. The affinity of Ag for X⁻ increases in the order Cl⁻ < Br⁻ < I⁻ and it may well happen that, with bromides or iodides, the affinity is so high that interaction of RX·⁻ with Ag becomes important or a change of mechanism from stepwise to concerted occurs.

Notes and references

† Cyclic voltammetry was performed by using a computer-controlled Autolab PGSTAT 12 potentiostat (EcoChemie, The Netherlands) in a conventional three electrode cell thermostated at 25 °C. All voltammograms were recorded in CH₃CN + 0.1 M Et₄NBF₄ using substrate concentrations of *ca.* 2 mM. The working electrodes were GC and Ag, while the counter and reference electrodes were Pt coil and saturated calomel electrode (SCE), respectively. Correction for the ohmic drop due to the solution resistance was always made by using the positive feedback method. A Ag electrode, freshly prepared according to a previously published procedure,[6a] was used in each experiment.

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Fig. 2 (a) Schematic diagram of the concerted dissociative ET at Ag; (b) reaction co-ordinate diagram: outer-sphere ET (dashed curve) and Ag-catalysed ET (solid curve). The subscripts sol and surf indicate molecules at the outer Helmholtz plane, the distance of closest approach to the electrode for non-specifically adsorbed species, and at the surface of the electrode, respectively.